# Chapter 22
# Photosynthesis

## SUMMARY


Section 22.1

- In eukaryotes, photosynthesis takes place in chloroplasts. The light reactions take place in the thylakoid membrane, a third membrane in chloroplasts in addition to the inner and outer membrane.
- The dark reactions of photosynthesis take place in the stroma, the space between the thylakoid membrane and the inner membrane of the chloroplast.
- The absorption of light by chlorophyll supplies the energy required for the reactions of photosynthesis. Several different kinds of chlorophyll are known. All have a tetrapyrrole ring structure similar to that of the porphyrins of heme, but they also have differences that affect the wavelength of light they absorb.
- This property allows more wavelengths of sunlight to be absorbed than would be the case with a single kind of chlorophyll.

Section 22.2

- Photosynthesis consists of two processes. The light reactions are electron transfer processes, in which water is oxidized to produce oxygen and $NADP^+$ is reduced to produce NADPH. The dark reactions are also electron transfer processes, but here carbon dioxide is reduced to carbohydrates.
- The path of electrons in the light reactions of photosynthesis can be considered to have three parts. The first is the transfer of electrons from water to the reaction-center chlorophyll of photosystem II.
- The second part is the transfer of electrons from the excited-state chlorophyll of photosystem II to an electron transport chain consisting of accessory pigments and cytochromes, with energy provided by absorption of a photon of light. The components of this electron transport chain resemble those of the mitochondrial electron transport chain; they pass the electrons to the reaction-center chlorophyll of photosystem I.
- The third and last part of the path of the electrons is their transfer from the excited-state chlorophyll of photosystem I to the ultimate electron acceptor $NADP^+$, producing NADPH; again, energy is provided by absorption of a photon of light.

Section 22.3

- The mechanism of ATP in chloroplasts closely resembles the process that takes place in mitochondria. The structure of the ATP synthase in chloroplasts is similar to that in mitochondria.

Section 22.4

- When photosynthesis first evolved, it was most likely to have been carried out by organisms that used compounds other than water as the primary electron source. Cyanobacteria were the first organisms to use water as the source of electrons, giving rise to the present oxygen-containing atmosphere.

Section 22.5

- In the dark reactions of photosynthesis, the fixation of carbon dioxide takes place when the key intermediate ribulose-1,5-bisphosphate reacts with carbon dioxide to produce two molecules of 3- phosphoglycerate. This reaction is catalyzed by the enzyme ribulose-1,5-bisphosphate carboxylase/ oxygenase (rubisco), one of the most abundant proteins in nature.
- The remainder of the dark reaction is the regeneration of ribulose-1,5-bisphosphate in the Calvin cycle.

Section 22.6

- In tropical plants, four-carbon compounds are frequently involved in the pathway of $CO_2$ fixation.
- This alternative pathway facilitates the movement of $CO_2$ into leaves and prevents water loss.

## LECTURE NOTES

This chapter is likely to take two lectures to complete, one for the light reactions, and one for the dark reactions. The light reactions of photosynthesis can be easily related to the respiratory electron transport chain of mitochondria, and the dark reactions to both gluconeogenesis and the pentose phosphate pathway. These strategies should ease students' understanding of these otherwise complex topics.

## LECTURE OUTLINE

I. Location of photosynthesis
    A. Chloroplasts
        1. grana
        2. thylakoid disks
        3. stroma
        4. thylakoid space
    B. Chlorophylls
        1. Structure and variants
        2. Absorption spectra
    C. Accessory pigments
    D. Photosystems
    E. Reaction Centers
II. Photosystems I & II
    A. Light vs. dark reactions
    B. Splitting of water at PS II
        1. Oxygen-evolving complex
        2. Electron transfers
        3. Phaeophytin
        4. Plastoquinone
        5. Cytochrome b6-f complex
        6. Plastocyanin

C. Reduction of NADP+ via PS I
    1. Reaction center electron transfers
    2. Ferredoxin
D. Cyclic electron transport
E. Photosystem structure

III. ATP production
    A. Proton gradient
    B. ATP synthase

IV. Evolutionary implications

V. The Dark Reactions
    A. Rubisco
        1. Ribulose-1,5-bisphosphate
        2. 3-phosphoglycerate
    B. Production of six-carbon sugars
    C. Regeneration of ribulose-1,5-bisphosphate

VI. $CO_2$ fixation in tropical plants

## ANSWERS TO PROBLEMS

### 22.1 Chloroplasts Are the Site of Photosynthesis

1. In the fall, the chlorophyll in leaves is lost, and the red and yellow colors of the accessory pigments become visible, accounting for fall foliage colors.
2. The bean sprouts are grown in the dark to prevent them from turning green; most customers will not purchase green sprouts.
3. Iron and manganese in chloroplasts; iron and copper in mitochondria. Note that all these are transition metals, which can easily undergo redox reactions.
4. Both chloroplasts and mitochondria have an inner and outer membrane. Both have their own DNA and ribosomes. Chloroplasts, however, have a third membrane, the thylakoid membrane.
5. Chlorophyll has a cyclopentanone ring fused to the tetrapyrrole ring, a feature that does not exist in heme. Chlorophyll contains magnesium, whereas heme contains iron. Chlorophyll has a long side chain based on isoprenoid units, which is not found in heme.
6. Only a relatively small portion of the visible spectrum is absorbed by chlorophylls. The accessory pigments absorb light at additional wavelengths. As a result, most of the visible spectrum can be harnessed in light-dependent reactions.
7. It is one more piece of evidence that is consistent with the evolution of chloroplasts from independent bacterial organisms.

### 22.2 Photosystems I and II and the Light Reactions of Photosynthesis

8. By and large, the synthesis of NADPH in chloroplasts is the reverse of NADH oxidation in mitochondria. The net electron flow in chloroplasts is the reverse of that in the mitochondria, although different carriers are involved.

9. When light impinges on the reaction center of *Rhodopseudomonas,* the special pair of chlorophylls there is raised to an excited energy level. An electron is passed from the special pair to accessory pigments, first pheophytin, then menaquinone, and finally to ubiquinone. The electron lost by the special pair of chlorophylls is replaced by a soluble cytochrome, which diffuses away. The separation of charge represents stored energy (see Figure 21.9).
10. In photosystem I and in photosystem II, light energy is needed to raise the reaction-center chlorophylls to a higher energy level. Energy is needed to generate strong enough reducing agents to pass electrons to the next of the series of components in the pathway.
11. No. Most chlorophylls are light-harvesting molecules that transfer energy to the special pair that takes part in the light reactions.
12. The electron transport chain in chloroplasts, like that in mitochondria, consists of proteins, such as plastocyanin, and protein complexes, such as the cytochrome $b_6$–$f$ complex. It also contains mobile electron carriers, such as pheophytin and plastoquinone (equivalent to coenzyme Q), which is also true of the mitochondrial electron transport chain.
13. Probably the electron transport chain in chloroplasts. Chloroplasts generate molecular oxygen; mitochondria use it. The early atmosphere almost certainly lacked molecular oxygen. Only when photosynthesis introduced oxygen into the atmosphere would oxygen be needed.
14. Electron transport and ATP production are coupled to each other by the same mechanism in mitochondria and chloroplasts. In both cases, the coupling depends on the generation of a proton gradient across the inner mitochondrial membrane or across the thylakoid membrane, as the case may be.
15. In mitochondria, both a proton gradient (chemical) and an electrochemical gradient (based on charge) are formed, both contributing to the total potential energy. In chloroplasts, only a proton gradient is formed, because ions move across the thylakoid membrane and neutralize charge. The proton gradient alone is considerably less efficient.
16. With very few exceptions, life directly or indirectly depends on photosynthesis. The electric current is the flow of electrons from water to $NADP^+$, a light-requiring process. The “current” continues in the light-independent reactions, with electrons flowing from NADPH to *bis*phosphoglycerate, which ultimately yields glucose.
17. Photosystem II requires more energy than photosystem I. The shorter wavelength of light means a higher frequency. Frequency, in turn, is directly proportional to energy.
18. It is quite reasonable to list reduction potentials for the electron-transfer reactions of photosynthesis. They are entirely analogous to the electron-transfer reactions in mitochondria, for which we listed standard reduction potentials in Chapter 20.
19. A photosynthetic reaction center is analogous to a battery because its reactions produce a charge separation. The charge separation is comparable to the stored energy of the battery.

20. The electron transport chains of mitochondria and chloroplasts are similar. In mitochondria, antimycin A inhibits electron transfer from cytochrome *b* to coenzyme Q in the Q cycle. By analogy, it can be argued that antimycin A inhibits electron flow from plastoquinone to cytochrome $b_6$–*f.* A Q cycle may also operate in chloroplasts.
21. Oxygen produced in photosynthesis comes from water. The oxygen-evolving complex is part of the series of electron-transfer reactions from water to NADPH. Carbon dioxide is involved in the dark reactions, which are different reactions that take place in another part of the chloroplast.
22. It is well established that the path of electrons in photosynthesis goes from photosystem II to photosystem I. The reason for the nomenclature is that photosystem I is easier to isolate than photosystem II and was studied more extensively at an earlier date.
23. It would take much work to establish the number of protons pumped across the thylakoid membrane. This is partly the result of experience with mitochondria and partly a prediction based on the greater complexity of structure in the chloroplast.
24. The oxygen-evolving complex of photosystem II passes through a series of five oxidation states (designated as $S_0$ through $S_4$) in the transfer of four electrons in the process of evolving oxygen (Figure 22.6). One electron is passed from water to photosystem II for each quantum of light. In the process, the components of the reaction center go successively through oxidation states $S_1$ through $S_4$. The $S_4$ decays spontaneously to the $S_0$ state and, in the process, oxidizes two water molecules to one oxygen molecule. Four protons are released simultaneously.
25. When the loosely bound cytochrome diffuses away, a charge separation is induced. This separation of charge represents stored energy.
26. The similarity of ATP synthase in chloroplasts and mitochondria supports the idea that both may have arisen from free-living bacteria.

## 22.3 Photosynthesis and ATP Production

27. In cyclic photophosphorylation, the excited chlorophyll of photosystem I passes electrons directly to the electron transport chain that normally links photosystem II to photosystem I. This electron transport chain is coupled to ATP production (see Figure 22.8).
28. Both depend on a proton gradient, resulting from the flow of electrons. In chloroplasts, protons come from the splitting of water to produce oxygen. In mitochondria, protons come from the oxidation of NADH and ultimately consume oxygen and produce water.
29. The proton gradient is created by the operation of the electron transport chain that links the two photosystems in noncyclic photophosphorylation.
30. ATP can be produced by chloroplasts in the absence of light if some way exists to form a proton gradient.
31. Cyclic photophosphorylation can take place when the plant needs ATP but does not have a great need for NADPH. Noncyclic photophosphorylation can take place when the plant needs both.

## 22.4 Evolutionary Implications of Photosynthesis with and without Oxygen

32. Many electron donors other than water are possible in photosynthesis. This is especially the case in bacteria, whose photosystems do not have strong enough oxidizing agents to oxidize water. Some of the alternative electron donors are $H_2S$ and organic compounds.
33. A prokaryotic organism that contains both chlorophyll *a* and chlorophyll *b* could be a relic of an evolutionary way station in the development of chloroplasts.

## 22.5 Dark Reactions of Photosynthesis Fix $CO_2$

34. Rubisco is the principal protein in chloroplasts in all green plants. This wide distribution makes it likely to be the most abundant protein in nature.
35. The amino acid sequence of the catalytic subunits of rubisco is encoded by chloroplast genes, whereas that of the regulatory subunits is encoded by nuclear genes.
36. Gluconeogenesis and the pentose phosphate pathway have a number of reactions similar to those of the dark reactions of photosynthesis.
37. From the standpoint of thermodynamics, the production of sugars in photosynthesis is the reverse of the complete oxidation of a sugar such as glucose to $CO_2$ and water. The complete oxidation reaction produces six moles of $CO_2$ for each mole of glucose oxidized. To get the energy change for the fixation of one mole of $CO_2$, change the sign of the energy for the complete oxidation of glucose and divide by 6.
38. Glucose synthesized by photosynthesis is not uniformly labeled because only one molecule of $CO_2$ is incorporated into each molecule of ribulose-1,5-*bis*phosphate, which then goes on to give rise to sugars.
39. If rubisco was one of the first protein enzymes to arise early in the evolution of life, it may not have the efficiency of protein enzymes that evolved later, when evolution was more dependent on modifying and adapting existing proteins.
40. Their DNA is circular. Their ribosomes are more like those of bacteria than those of eukaryotes. Their aminoacyl-tRNA synthetases use bacterial tRNAs but not eukaryotic tRNAs. In general, they do not have introns in their genomes. Their mRNA uses a Shine-Dalgarno sequence.
41. The pathway borrows heavily from the nonoxidative branch of the pentose phosphate pathway and from gluconeogenesis. Without doubt, the pathways yield sugars as well as NADPH for reductive biosynthesis. Thus, only a few new enzymes would have to evolve through mutations to enable the complete Calvin cycle to function.
42. Atmospheric oxygen is a consequence of photosynthesis. Rubisco evolved before there was a significant amount of oxygen in the atmosphere.
43. The condensation of ribulose-1,5-*bis*phosphate with carbon dioxide to form two molecules of 3-phosphoglycerate is the actual carbon dioxide fixation. The rest of the Calvin cycle regenerates ribulose-1,5-*bis*phosphate.
44. Organisms would need only a few mutations giving rise to the enzymes unique to the Calvin cycle. The rest of the pathway is already in place.
45. Six molecules of carbon dioxide fixed in the Calvin cycle do not end up in the same glucose molecule. However, labeling experiments show that six carbon

atoms are incorporated into sugars for every six carbon dioxide molecules that enter the Calvin cycle.

## 22.6 $CO_2$ Fixation in Tropical Plants

46. In tropical plants, the $C_4$ pathway is operative in addition to the Calvin cycle.
47. In $C_4$ plants, when $CO_2$ enters the leaf through pores in the outer cells, it reacts first with phosphoenolpyruvate to produce oxaloacetate and $P_i$ in the mesophyll cells of the leaf. Oxaloacetate is reduced to malate, with the concomitant oxidation of NADPH. Malate is then transported to the bundle-sheath cells (the next layer) through channels that connect two kinds of cells. These reactions do not take place in $C_3$ plants.
48. Photorespiration is a pathway in which glycolate is a substrate oxidized by rubisco acting as an oxygenase, rather than as a carboxylase. Photorespiration is not completely understood.
49. Three reasons come to mind. (1) Light energy is usually not limiting. (2) The plants have small pores to prevent water loss, but this also limits $CO_2$ uptake. (3) The $C_4$ pathway allows for increasing the $CO_2$ concentration in the inner chloroplast, which would not be otherwise possible with the small pores.
50. Most plants would be more productive in the absence of photorespiration. There is another side to this picture, however. The oxygenase activity appears to be an unavoidable, wasteful activity of rubisco. Photorespiration is a salvage pathway that saves some of the carbon that would be lost due to the oxygenase activity of rubisco. Photorespiration is essential to plants even though the plant pays the price in loss of ATP and reducing power; mutations that affect this pathway can be lethal.